Flammability Properties of Hydrocarbon Fuels

Part 4 - The Significance of Flash Point as an Indicator of the Flammability Hazard of Hydrocarbon Fuels

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PREVIOUS REPORTS IN THIS SERIES

"Part 1 — Interrelations of Flammability Properties of n-Alkanes in Air," W. A. Affens, NRL Report 6270, May 25, 1965

"Part 2 — The Importance of Volatile Components at Low Concentration on the Flammability of Liquid Fuels," W. A. Affens, NRL Report 6578, July 10, 1967.

"Part 3 — Flammability Properties of Hydrocarbon Solutions in Air," W. A. Affens, NRL Report 6617, Nov. 21, 1967

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ABSTRACT

The significance of flash point as a measurement of flammability hazard of flammable liquids and multicomponent solutions and its experimental determination were evaluated. Experimentally determined flash points were found to be in good agreement with values which were calculated from theoretical principles. The results confirm that liquid hydrocarbon solutions follow the laws of Dalton, Raoult, and LeChatelier governing the vapor pressure, composition, and flammability limits above a liquid of two or more components, and also confirm the concept of flash point as that temperature at which the vapor concentration above a liquid is equal to that at its lower flammability limit.

PROBLEM STATUS

This is an interim report. Work on the problem is continuing.

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FLAMMABILITY PROPERTIES OF HYDROCARBON FUELS

Part 4 — The Significance of Flash Point as an Indicator of the Flammability Hazard of Hydrocarbon Fuels

INTRODUCTION

Flash point is the best known and most widely measured flammability property for evaluating the flammability hazard of combustible liquids and is used as an important criterion for classifying these liquids according to their fire hazard rating. For example the National Fire Protection Association [1] classifies liquids with flash points below 100°F as "Flammable Liquids, Class I," and those with flash points of 100°F and above, but below 140°F as "Flammable Liquids, Class II." Liquids with flash points of 140°F and above are classified as "Combustible Liquids." There are numerous other systems in the United States and elsewhere for classifying combustible liquids [2], and in all of these systems flash point is a key factor [1-4]. For similar purposes the Navy sets flash point requirements in the specifications for many of its fuels, particularly those which are used in large quantities aboard ships. For example the military specifications for Navy Special fuel oil [5] and Navy Distillate fuel [6] require that these fuels have a minimum flash point of 150°F. JP-5 jet fuel, which is used by carrier-based aircraft, is required to have a flash point minimum of 140°F [7]. These and other requirements are incorporated into fuel specifications as a means of reducing the fire hazard in the storage, transportation, and use of these fuels.

The flammability hazard of a given fuel, to a large degree, is a function of its vapor pressure and hence of its temperature. Most important is the particular temperature at which the liquid will produce a flammable vapor mixture with air. If this temperature is known, one has important information for evaluating whether the fuel is hazardous or not under a given set of conditions. As will be shown in what follows, this temperature represents in concept a fundamental or ideal definition of flash point.

FLASH POINT

Fundamentally the flash point of a flammable liquid is the minimum temperature at which its vapor pressure is sufficient to form a flammable vapor-air mixture at 1 atmosphere pressure [3,8-10]. In other words it is that temperature at which the equilibrium vapor concentration above the liquid is equivalent to that at its lower flammability limit. The flash point is thus the same as the lower flammability temperature limit. There are actually two flash points, a *lower flash point* t_L and an *upper flash point* t_U corresponding to the lower and upper flammability temperature limits. The unmodified expression "flash point," as is usually the custom, refers to the lower flash point.

This temperature represents the idealized flash point of a particular flammable liquid but, because of equilibrium and other considerations, may differ somewhat from experimentally determined values. For similar reasons experimentally determined flash points of the same liquid may differ. Despite these discrepancies experimentally determined flash points are extremely valuable information, since they can give guidance as to what temperature ranges a given flammable liquid may be hazardous. Furthermore a flash point can be used to detect contamination of a relatively nonflammable fluid by a more flammable one.

Experimentally determined, flash points depend to a high degree on the type of apparatus and the method used for its determination, such as a closed or open cup and the rate of heating. From the experimental viewpoint flash point may be defined as "the temperature to which the product must be heated under the specified conditions of the method to give off sufficient vapor to form a mixture with air that can be ignited momentarily by a specified flame" [11].

The term *fire point* is used to define the temperature at which the product will burn continuously under the same prescribed conditions and is determined in an open-cup (open to the atmosphere) apparatus. In general, closed-cup flash points are lower and more reliable than those obtained by open-cup methods [3,12]. This might be expected, since the vapors in a closed-cup apparatus are likely to be closer to equilibrium than those in an open cup, where diffusion to the outside can occur. There are cases however for which the open-cup method might be more meaningful and therefore preferable. This would be true, for example, in evaluating the flammability hazard resulting from a spill of a mixture of a flammable liquid with an inert volatile diluent, such as ethylene oxide and halocarbon. In a closed space (assuming excess liquid) the presence of the inert diluent vapors (halocarbon) would tend to inhibit the flammability of the vapor-air mixture by increasing its lower flammability limit [13], so that a closed-cup flash point might be higher and more meaningful. If enough halocarbon were present, it would even render the vapor mixture nonflammable. In an open space however the inert diluent might dif.use away, and in that case the mixture would be more flammable than with the inert diluent present, so that the open-cup flash point would be lower and thus more conservative [3] and meaningful than the closed cup.

In the case of a spill in an open space of a multicomponent mixture of flammable components containing no inert diluent, the more volatile low-flash-point components would diffuse away with time, leaving behind the less volatile material. This is sometimes called weathering. In such a case it can be considered that the closed-cup flash point would be more conservative and less meaningful than the open-cup flash point. However, in the more frequently encountered situations, we are concerned with the flammability hazard in closed or partly closed spaces, such as in fuel tanks and the like, because these usually represent the areas of greatest potential hazard. As a rule closed-cup flash points would give a better measure of what might be expected in these situations and hence would be a better index of safety. Furthermore it would be expected that closed-cup flash points should be more accurate and in closer agreement with flash points calculated from fundamental principles.

In a previous report [14] equations were derived which make it possible to predict flammability properties and particularly the flash points of liquid hydrocarbon solutions in air from the properties and proportions of the individual components. These equations were based on the application of Raoult's and Dalton's laws governing vapor pressure and composition above a solution of two or more liquid hydrocarbons to LeChatelier's rule governing the flammability limits of vapor mixtures.

The flash point temperature of a liquid solution of two or more components, although a simple determination in the laboratory, is a complex flammability property. Its estimation from fundamental principles involves the simultaneous interrelation of at least six relationships. In addition to the three relationships of Raoult, Dalton, and LeChatelier mentioned, two others govern the variations of both vapor pressure and lower flammability limit with temperature [14]. Finally there is the relationship which is based on the conceptual definition or meaning of flash point temperature [8] as that temperature at which the vapor pressure (or its equivalent, concentration) is equal to that at the lower flammability limit. An experimental evaluation of a calculated flash point temperature of a multicomponent hydrocarbon solution would therefore be a simultaneous test of the six individual relationships.

The equation derived earlier (in Part 3 of this series [14]) for calculating the flash point of a multicomponent liquid hydrocarbon solution $\Theta_{L,M}$ from the flash point $\Theta_{L,i}$ and proportions x_i (mole fraction) of the individual components is

$$\sum_i \left[x_i 10^{a_i} (1642 - \Theta_{L,i}) / (1642 - \Theta_{L,M}) \right] = 1, \tag{1}$$

where

$$a_i = m_i (\Theta_{L,i} - \Theta_{L,M}) / \Theta_{L,i} \Theta_{L,M},$$

$$\Theta = t°C + 230,$$

and M_i is a constant (from a semilogarithmic plot of vapor pressure versus temperature for the component i). The symbols used in this report are defined in the Nomenclature at the end of the report and have been altered slightly from that of the original derivation for simplification. For a two-component solution of ingredients A and B, for example, Eq. (1) becomes

$$\left[(1642 - \Theta_{L,A}) x_A / (1642 - \Theta_{L,M}) \right] 10^{a_A} + \left[(1642 - \Theta_{L,B}) x_B / (1642 - \Theta_{L,M}) \right] 10^{a_B} = 1, \tag{2}$$

where specific values a_A and a_B are calculated for the two components. The number of terms in the equation is equal to the number of components in the solution. If the concentration of a given component is expressed in percent by volume c_i, which is generally the case, it is related to mole fraction as follows:

$$x_i = (d_i c_i / M_i) / \sum_i (d_i c_i / M_i), \tag{3}$$

where d_i is the density and M_i is the molecular weight of a given component.

The purpose of the present work is to verify experimentally the preceding equations as applied to hydrocarbon solutions.

EXPERIMENTAL METHOD AND RESULTS

Choice of Method for Determining Flash Point

There are numerous methods for determining flash point, of which four [15-18] are standard in the United States. The flash points of three hydrocarbon samples and six jet fuel samples were determined by these four methods, and comparative data are given in Table 1. With one minor exception (JP-4 jet fuel, No. J-354), the Tag closed-cup apparatus [15] gave the lowest

Table 1
Comparison of Flash Point Temperatures by Different Methods

Fuel	Flash Point Temperature, t_L (°C)			
	Closed Cup		Open Cup	
	Tag [15]	Pensky-Martens [16]	Tag [17]	Cleveland [18]
$n-C_8H_{18}$	15	17	19	31
$n-C_{11}H_{24}$	64	69	71	78
$95\%(v/v)C_{11}H_{24}+5\%C_8H_{18}$	53	57	61	70
JP-4 (Andrews)	−10	−14	−13	−2
JP-4 (No. J-354)	−6	−8	−4	9
JP-5 (No. J-434)	58	60	70	78
JP-5 (No. J-437)	57	62	68	71
JP-5 (No. J-439)	60	61	71	77
JP-5 (No. J-441)	58	60	68	76

results. The reason for the lower flash points by the Tag closed-cup method is probably due chiefly to the lower heating rate by this method compared with that of the Pensky-Martens method. Under these circumstances the vapor-air mixture in the ullage space above the liquid would be closer to being in equilibrium with the liquid. From the point of view of assessing flammability hazard, and from design and experimental considerations, it was decided to use the Tag closed-cup apparatus in this work. The hydrocarbons were obtained from the Phillips Petroleum Company and specified to have a minimum purity of 99 mol-percent.

Flash Points of Pure *n*-Alkanes

The method was first tested against some pure hydrocarbons, and the results are given in Table 2 along with average literature data [8] and calculated data [8] for comparison. The experimental results, although slightly higher, are in good agreement with both the literature average and calculated data.

Flash Points of Multicomponent Solutions

Two series of binary solutions covering the entire concentration ranges of *n*-heptane and *n*- octane, each in *n*-undecane, were tested. The results, given in Fig. 1, are plotted against the curves which were based on Eq. (2). It is seen that the experimental results are in excellent agreement with the calculated values.

Eight additional multicomponent solutions were prepared from two to six components, and the flash points are shown in Table 3. Here also the results are in good agreement with calculated values.

Table 2
Flash Point Temperatures of Pure n-Alkanes

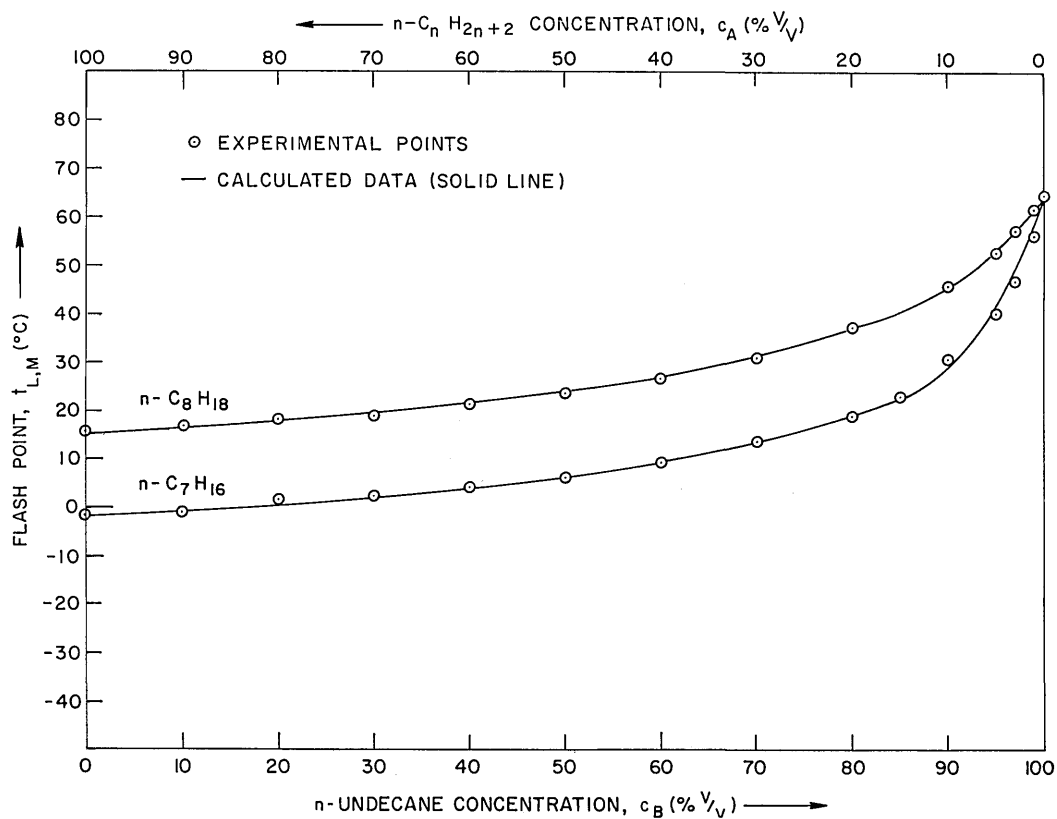| Carbon Number, n, $n\text{-}C_nH_{2n+2}$	Flash Point Temperature (°C)		
	Calculated (Graphical) [8]	Literature Average [8]	Experimental (Tag Closed Cup) [15]
7	−6	−3	−1
8	13	14	15
9	31	31	33
10	47	46	48
11	62	64	64
12	76	74	79

Fig. 1 — Calculated and experimental flash points of binary
solutions of n-heptane and n-octane in n-undecane

TABLE 3

Flash Point Temperatures of Multicomponent
n-Alkane Solutions

n-Alkane ($n\text{-}C_nH_{2n+2}$) Concentration, c_i (% v/v)						Flash Point, $t_{L,M}$ (°C)	
$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 11$	$n = 12$	Calculated	Experimental*
50	50	—	—	—	—	5	2
33.3	33.3	—	—	33.3	—	10	10
25	15	—	—	60	—	15	14
20	20	—	—	60	—	17	16
5	5	—	—	90	—	37	37
25	—	25	—	25	25	17	15
20	20	20	—	20	20	16	16
15	15	15	15	25	15	20	20

*Tag closed-cup method [15]

DISCUSSION AND CONCLUSIONS

The good agreement of experimental flash points with calculated values for pure hydro-carbons and their multicomponent solutions demonstrates that flammability properties may be treated on a basis of fundamentals from physical chemistry. The concept of flash point as that temperature at which the equilibrium vapor composition above a liquid is equivalent to that at its lower flammability limit has been demonstrated to be valid. In the case of solutions of two or more flammable liquids the problem of defining these concepts has been shown to be more complex and requires an additional concept. For solutions the flash point is that tempera-ture at which the vapor pressure of each of the flammable volatile components is such that the composition of the vapor-air mixture above the liquid is flammable in accordance with Le-Chatelier's rule [14]. The experimental results confirm that liquid hydrocarbon solutions follow the laws of Dalton, Raoult, and LeChatelier governing the vapor pressure, composition, and flammability limits above a solution of two or more components.

An important observation from the derived equations for flash point and the experimental confirmation is that a very small amount of a highly volatile flammable contaminant, such as JP-4 jet fuel, in a relatively nonflammable fuel, such as JP-5, will reduce its flash point markedly and may make it much more flammable. The precise relationships have been derived for rela-tively simple solutions of pure hydrocarbons, but the concepts they imply are applicable to more complex mixtures, such as gasoline, jet fuels, and Navy Distillate fuels.

It has also been demonstrated in this work that flash point is an important and meaningful flammability property and that its meaning and concept can be considered in terms of funda-mental principles. Although experimental flash point results depend to a large degree on the

apparatus and method employed, they give important and useful flammability information when interpreted carefully. This common and simple laboratory test certainly deserves more dignity than is usually attributed to it.

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NOMENCLATURE

t_L (t_F)* = flash point, °C

Θ_L (T') = $t_L + 230$

Θ = $t°C + 230$

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*Symbols used in earlier reports and publications [8,14] are shown in parentheses.

$c\ (X)$ = concentration of fuel component by volume in a liquid fuel mixture, $\%\ v/v$

$x\ (N)$ = mole fraction of fuel component in a liquid fuel mixture

d = density, g/cm^3

$M\ (\overline{M})$ = molecular weight, $g/g-mol$

m = slope from a plot of log p vs $1/\Theta$ in the Antoine equation

Subscripts

L = at flash point

i = general component

A, B, etc. = specific component

M = multicomponent mixture

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